Supplementary Information

Atomic layer deposition of a Sb_2Se_3 Photo-absorber Layer using Selenium Dimethyldithiocarbamate as new Se precursor

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SI-1: Literature review of Se precursors investigated for metal selenide ALD

Sr. No	Se Precursor	Vapor pressure	Decomposition temp	Safety quotient	Availability	Reference	Note
1.	H_2Se	High (gaseous precursor		Extremely toxic and flammable	Limited (due to toxicity)	[1,2]	NA
2.	Diethylselenium + H_2	NA	Decomposed Se vapors only	Extremely toxic and flammable	Commercially available but with limited usage	[3]	Not a ideal ALD precursor. Limited ALE report. Not suitable for most exchange reaction with most often used metal precursors
3.	Se + H_2	NA	NA	Extremely toxic and flammable	Commercially available but with limited usage	[4]	Not an ideal ALD precursor. Limited ALE report. Not suitable for most exchange reaction with most often used metal precursors
4.	$(R_3Si)_2Se$	Data not available	Data not available	Data not available	Commercially NOT available	[5,6]	Lab scale synthesis reported with 83% yield.
5.	Selenium Dimethyldithiocarbamate	Low, solid precursor	200°C	NO, unless exposed to large amount	YES	This report	

SI-2: Substrate preparation:

Commercially available TEC 7 fluorine doped tin oxide (FTO) coated conducting glass substrates (from Dyesol, Australia) are used as substrates for *ex-situ* measurement purposes. The substrates are ultrasonically cleaned in acetone, alconox solution, DI water and isopropyl alcohol (IPA) sequentially for 15 min each. Dense TiO_2 (d-TiO_2) blocking layer is then spin coated at the spin program of 2500 rpm for 60 sec and then sintered in air at 500°C for 1 hr followed by natural cooling. The solution used for d-TiO_2 spin coating is prepared in two steps where step one contains 369 µL of TTIP to 2.53 mL of IPA stirred vigorously for 5 min. In the second step, a solution of 35 µl HCl in 2.53 mL of IPA is then added dropwise and stirred for 2 hours before spin coating on the FTO substrates. A mesoporous TiO_2 (p-TiO_2) is then spin coated on d-TiO_2 layer using a commercially available 30 NRD titania paste (from Dyesol, Australia) where the paste is diluted in an anhydrous ethanol (from Sigma Aldrich) in 1:3 weight ratio and spin coated at 1000 rpm for 60 sec. The samples are then sintered again in air at 500°C for 1 hr followed by natural cooling.

SI-3: Isothermal TG/DTA:

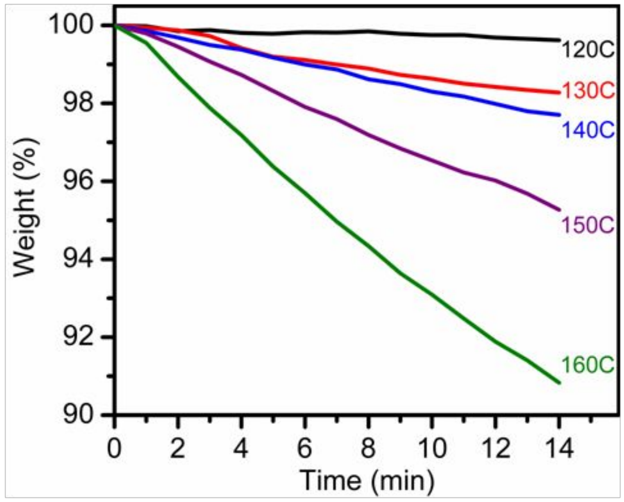

Figure SI-1: Isothermal TGA data for SDMDTC in N_2 ambience at different temperatures namely 120°C, 130°C, 140°C, 150°C and 160°C.

SI-4: Sb_2Se_3 self-saturation study by in-situ QCM:

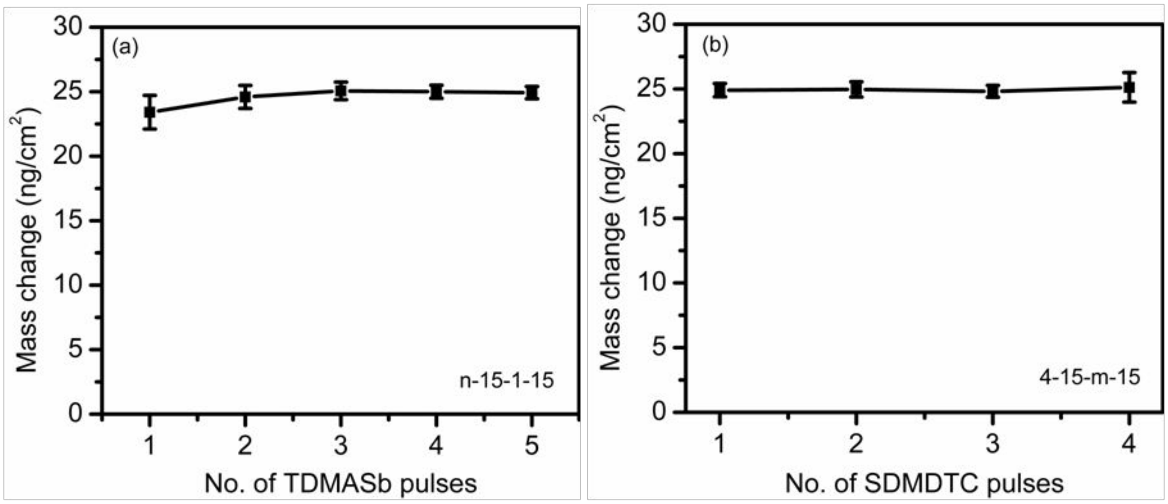

Figure SI-2: Mass changes versus precursor exposures of (a) TDMASb and (b) SDMDTC for self-saturation studies during Sb_2Se_3 deposition.

Figure SI-2(a) represents the mass gain per cycle as a function of TDMASb exposure where single pulse of 1 sec is kept constant in the SDMDTC half cycle. The surface sites are seen to saturate completely with minimum of 3 TDMASb exposures of 1 sec each. However, growth rate seems to saturate with a single exposure of 1 sec of SDMDTC in the second half cycle as shown in figure SI-2(b). Hence, 3 exposures of TDMASb and single exposure of SDMDTC are required to saturate the surface reactions for each ALD cycle producing a steady state mass gain of ca. 25 ng/cm^2. This corresponds to the growth rate of ca. 0.28 Å/cyl as the saturated growth of Sb_2Se_3.

SI-5: Deconvolution of Sb 3*d* and Se 3*d* core levels by HR-XPS:

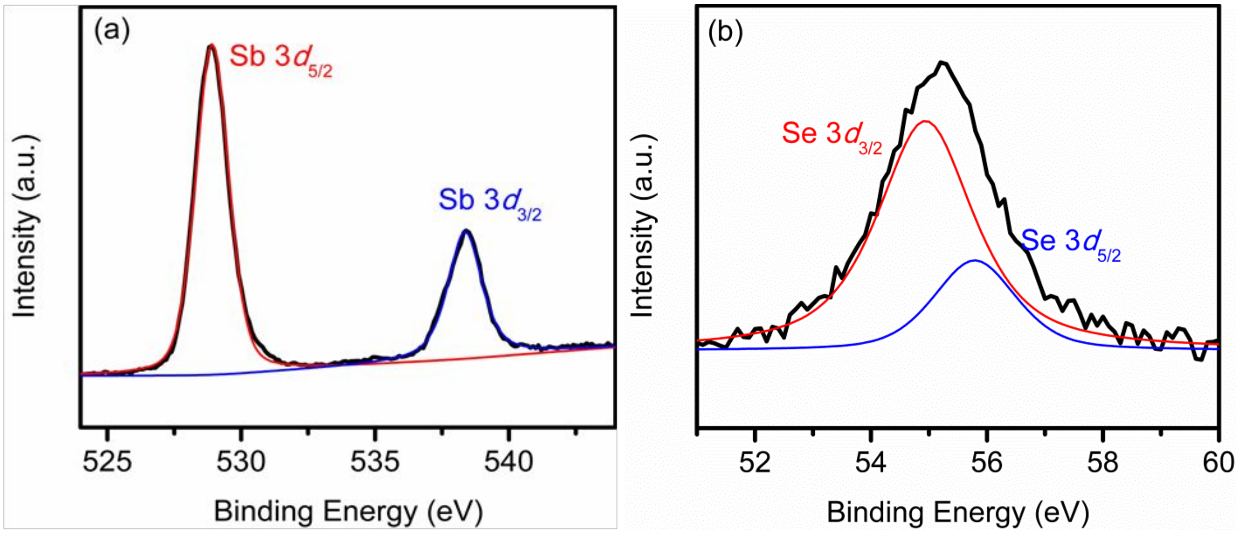

Figure SI-3: Deconvolution of high resolution core scan of (a) Sb 3*d* and (b) Se 3*d* for as-deposited samples.

SI-6: Optical transmission and Tauc plot for as-deposited Sb_2Se_3 thin films:

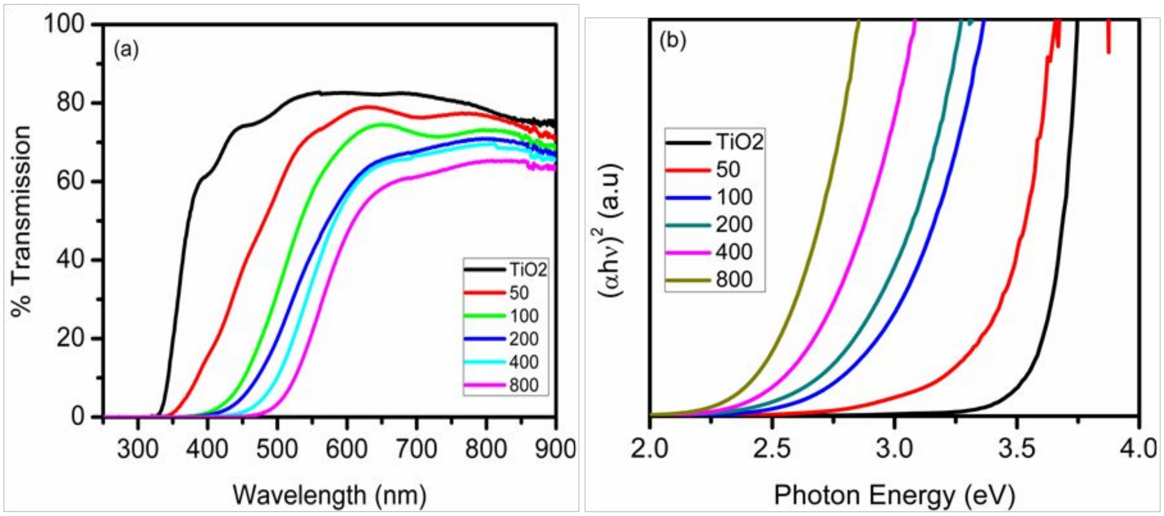

Figure SI-4: (a) Optical transmission spectra of bare and ALD Sb_2Se_3 coated TiO_2 films at 150°C and (b) the corresponding Tauc plot with n =2 for direct band gap calculations.

SI-7: Urbach energy calculation:

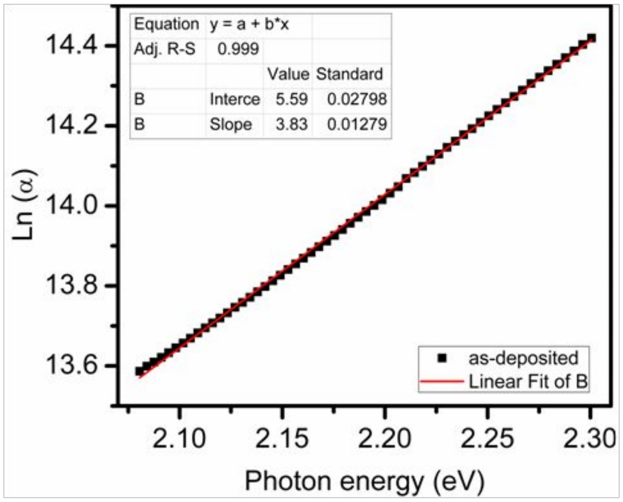

Figure SI-5: Linear fitting curve for the Urbach energy calculation of as-deposited Sb_2Se_3 ALD grown films.

SI-8: Reference Xe light spectra:

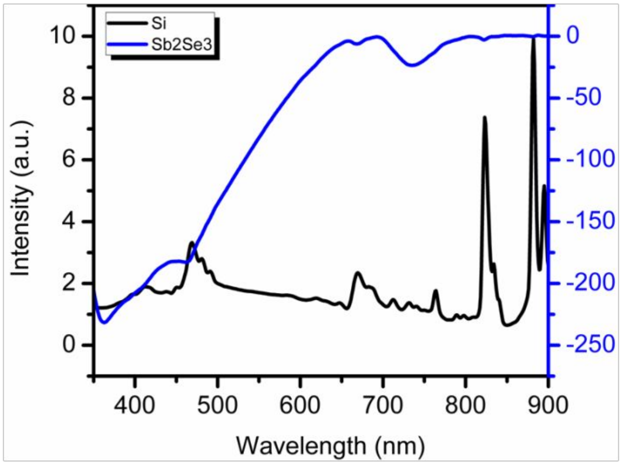

Figure SI-6: Xe light spectra measured by Si detector (black) and Sb_2Se_3 SPS spectra (blue) under the monochromatic light in the wavelength range of 900-300 nm.

REFERENCES

1. Browning, R.; Kuperman, N.; Moon, B.; Solanki, R. Atomic Layer Growth of InSe and Sb_2Se_3 Layered Semiconductors and Their Heterostructure. *Electronics* **2017,** *6* (2), 27.
2. Hsu, C. T. Epitaxial Growth of II–VI Compound Semiconductors by Atomic Layer Epitaxy. *Thin Solid Films* **1998,** *335* (1), 284-291.
3. Kimura, R.; Konagai, M.; Takahashi, K. Atomic Layer Epitaxy of ZnSe on GaAs(100) by Metalorganic Molecular Beam Epitaxy. *Journal of Crystal Growth* **1992,** *116* (3), 283-288.
4. Guziewicz, E.; Godlewski, M.; Kopalko, K.; Łusakowska, E.; Dynowska, E.; Guziewicz, M.; Godlewski, M. M.; Phillips, M. Atomic Layer Deposition of Thin Films of ZnSe—Structural and Optical Characterization. *Thin Solid Films* **2004,** *446* (2), 172-177.
5. Pore, V.; Hatanpää, T.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of Metal Tellurides and Selenides Using Alkylsilyl Compounds of Tellurium and Selenium. *Journal of the American Chemical Society* **2009,** *131* (10), 3478-3480.
6. Sarnet, T.; Hatanpaa, T.; Vehkamaki, M.; Flyktman, T.; Ahopelto, J.; Mizohata, K.; Ritala, M.; Leskela, M. $(Et_3Si)_2Se$ as a Precursor for Atomic Layer Deposition: Growth Analysis of Thermoelectric Bi_2Se_3. *Journal of Materials Chemistry C* **2015,** *3* (18), 4820-4828.